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# Mesomorphic behaviour of stearic acid in DMS

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**Abstract** : The mixture of stearic acid in DMS (dimethyl sulphoxide) exhibits non-aqueous lyotropic phase Observed numerous optical textures like batonnets, fan, oily streaks, droplets, X-ray and DSC (Differential Scanning Calorimeter) recordings of these mixtures indicate the existence of lamellar phase

**Keywords** : Stearic acid, DMS, lamellar phase

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Lyotropic liquid crystals are formed by the action of a solvent on an amphiphilic substance [1]. Non-aqueous lyotropic liquid crystals have been found in a multitude of polymer/organic solvent combinations [2–7]. Since these liquid crystals obviously present a novelty in the field, we find there is a continued interest in investigations of such systems. Recently, we have reported the mesomorphic behaviour of lauric acid in cetyl alcohol [8]. In this paper, we have investigated the mesomorphic behaviour of stearic acid (SA) in dimethyl sulphoxide (DMS).

Stearic acid was obtained from M/s Sigma, Bombay and was used without further purification. Analar grade DMS supplied by M/s Sisco Research Laboratory was used as a solvent. Mixtures in the range 10 to 90% by weight of stearic acid in DMS were prepared with care since DMS is hygroscopic. All samples (10 → 90% of SA in DMS), when observed under a polarizing microscope, show room temperature lyotropic mesomorphism. Texture observations were carried out using Leitz Orthoplan polarizing microscope by allowing the sample to cool slowly from the isotropic phase at the rate of 2°/min.

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The sequence of textures observed for all concentrations in the cooling mode was similar in nature and they are droplets, batonnets, fan-like texture and focal conics at room temperature and Figure 1 shows fan texture observed in 20% of SA in DMS. If the sample is left at room temperature for nearly two to three hours, almost all the samples show sanded texture. The transition temperature from mesomorphic to isotropic phase was determined using Leitz Orthoplan polarizing microscope in conjunction with a hot stage. DSC recordings for the samples with 20, 40, 60% of SA in DMS showed additional small peaks. However, we were unable to see the corresponding changes in the textures. In fact, there is no change in textures except for few insignificant changes. Unfortunately, we could not resolve this problem either with X-ray recording as our temperature controller had an accuracy of ± 2°C over the entire region of the sample. Average enthalpy change for different concentrations and corresponding average transition temperatures are given in Table 1. It can be noticed from the Table 1, that the enthalpy increases with increase in concentration of stearic acid in agreement with the concept that higher concentration of SA leads to more ordered phase.

**Table 1.** DSC, X-ray, refractive index, orientational order of SA in DMS and cell parameters for different concentrations.

| Sample | Transition* | Δ H | $n_e^{\dagger}$ | $n_0^{\dagger}$ | $\rho^{\dagger}$ | $S^{\dagger}$ | X-ray results$^{+,\dagger}$ | |
|---|---|---|---|---|---|---|---|---|
| 10% | 44.0 | 18 5 | — | — | — | — | a = 24 1, b = 36 9 | c = 14 3 |
| 20% | 48 0 | 5 6 | 1 510 | 1 475 | 1 091 | 0 78 | $\alpha$ = 96.3, $\beta$ = 87 1 | $\gamma$ = 118 9 |
| 30% | 52 0 | 11 0 | 1.500 | 1 468 | 1 060 | 0 48 | $2\theta_{exp}$ | $2\theta_{cal}$ |
| 40% | 45.3 | 13 0 | 1.510 | 1.476 | 1.043 | 0.41 | 8.8 | 8.8 |
| 50% | 49 2 | 18.0 | 1.508 | 1 477 | 1.026 | 0.30 | 13.4 | 13 4 |
| 60% | 50.4 | 11.0 | 1.499 | 1.473 | 1 024 | 0.25 | 20.3 | 20.4 |
| 70% | 58.8 | 32.0 | — | — | — | — | 28.2 | 28.4 |
| 80% | 57.2 | 26.0 | — | — | — | — | 31.6 | 31 6 |
| 90% | 62.5 | 38.0 | — | — | — | — | 34.3 | 34.3 |

* temperature in °C from mesomorphic to isotropic phase + common for all concentrations, † at room temperature (in mesomorphic phase) and ΔH in cals/gm

Observed X-ray-diffraction rings for all the concentration range, are given in Table 1. There is absolutely no variation in *d*-spacing of the inner ring with concentration. The number of X-ray diffraction rings observed vary with concentration but the *d*-spacings remain the same. We are also certain that the sample at room temperature is not in a crystalline phase but a non-aqueous lyotropic phase. Since none of the ratio methods suggested by earlier investigators could account for the observed *d*-spacings, we have used a simple multi-dimensional minimization program (SIMPLEX) which starts with an initial [9] approximate set of cell parameters and finally obtaines a refined set of cell parameters

***Plate I***

**Figure 1.** Micro texture photograph of 20% of SA in DMS (108x temp 45.0°C).

which will fit the observed Bragg reflections to within ± 1.2% of the mean value and the cell parameters are given in Table 1 along with calculated and experimental Bragg angles. It is evident that the cell parameters represent a slightly distorted hexagonal symmetry and this has been observed for the whole range of concentrations. This clearly indicates that the system is ordered distorted hexagonal-type lamellar mesophase.

Refractive indices ($n_e$, $n_0$, for $\lambda$ 5893*A*) and density measurements at different temperatures for different concentrations have also been carried out with an intention of studying the variation of the order parameter $S$ of the *SA* molecule in the non-aqueous lyotropic system using the following equations with an approximation that anisotropy of DMS is very small compared to *SA*. Lorenz–Lorentz relation for extra-ordinary refractive index for SA in DMS is given by

$$\frac{n_e^2 - 1}{n_e^2 + 2} = \frac{3}{4\pi N}\left[\omega_{SA}\overline{\alpha_{SA}} + \omega_{DMS}\overline{\alpha_{DMS}} + 2/3\{\omega_{SA}\Delta\alpha_{SA}S\}\right], \tag{1}$$

$$\frac{n_0^2 - 1}{n_0^2 + 2} = \frac{3}{4\pi N}\left[\omega_{SA}\overline{\alpha_{SA}} + \omega_{DMS}\overline{\alpha_{DMS}} - 1/3\{\omega_{SA}\Delta\alpha_{SA}S\}\right]. \tag{2}$$

Subtracting eq. (2) from (1) we get,

$$\left[\frac{n_e^2 - 1}{n_e^2 + 2} - \frac{n_0^2 - 1}{n_0^2 + 2}\right] = \frac{3}{4\pi N}\omega_{SA}\Delta\alpha_{SA}S], \tag{3}$$

which can be used for finding the orientational order of *SA* molecule in the lyotropic system. With increase in the concentration of *SA*, this order decreases and with temperature, this remains almost constant within the experimental accuracy and such linear variation of $S$ in terms of quadrupole splittings has been observed in the case of Lecithin/ethylene glycol lamellar liquid crystal [10].

From these X-ray and optical studies, we conclude that the mixtures of SA in DMS exhibit slightly distorted hexagonal non-aqueous lyotropic system.

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